Asian Journal of Chemistry Vol. 22, No. 7 (2010), 5077-5085

Study on Biodegradable Random Copolyesters Derived From 1,4-Butane Diol, Terephthalic Acid and Adipic Acid/Sebacic Acid

V. JAISANKAR*, R. NANTHINI†, M. KARUNANIDHI† and A. RAVI†
Department of Chemistry, Presidency College, Chennai-600 005, India
Fax: (91)(44)28235297; E-mail: vjaisankar@gmai.com

A series of high molecular weight polyesters, poly(butylene adipate-co-butylene terephthalate) (PBAT) and poly(butylene sebacate-co-butylene terephthalate) (PBSeT) were synthesized by a direct melt polycondensation method using titanium tetraisopropoxide (TTiPO) as catalyst. The structure, average molecular weights and physical properties of the resulting random copolyesters were analyzed by IR, ^{1}H NMR, gel permeation chromatography, viscosity measurements, differential scanning calorimetry and X-ray diffraction studies. The effect of copolymer composition on the physical and thermal properties, as well as enzymatic degradation was investigated. The enzymatic degradation was performed in a buffer solution with enzyme *Candida cylindracea* lipase. The rate of enzymatic degradation of these polyesters were compared. The poly(butylene adipate-co-butylene terephthalate) has highest enzymatic degradation rate than poly(butylene sebacate-co-butylene terephthalate). It appears that the key factor affecting material degradation was its crystallinity.

Key Words: Biodegradation, Aliphatic-aromatic copolyesters, Melt polycondensation, Enzymatic degradation.

INTRODUCTION

In recent years, considerable efforts have been taken on the synthesis and characterization of new biodegradable polymers with potential applications as both commodity and speciality materials[1,2]. Furthermore, there are a number of reports concerning aliphatic polyesters due to their favourable features of biodegradability and biocompatibility[3-5]. Based on the condensation reaction of diol and dicarboxylic acid initially reported by Caroethers[6], aliphatic polyesters such as poly(butylene succinate) (PBS), poly(ethylene succinate) (PES), poly(butylene adipate) (PBA) and so on, have been synthesized and characterized[7-11].

The development of biodegradable polymers for packaging, sanitary and agricultural uses would partially solve the problem of plastic waste accumulation. Aliphatic polyesters are the most promising biodegradable materials because they are readily susceptible to biological attack[12]. Poly (β-hydroxy butyrate) and poly(lactic acid) have been extensively investigated as biodegradable polyesters and have a large

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†Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India.

number of biomedical applications such as absorbable bone plates, some surgical fixation devices, bioabsorbable surgical sutures and carriers for the controlled release of drugs. These aliphatic polyesters are commercially produced either by microorganisms, ring-opening polymerization of lactones or ring-opening poly addition of cyclic dimers[13-15].

Mochizuchi *et al.*[16] reported the synthesis of high molecular weight biodegradable poly(butylene succinate-co-ethylene succinate)s by direct polycondensation reaction of diols and diacids in presence of a highly effective catalyst. Djonlagic *et al.*[17] reported the synthesis of biodegradable poly(butylene succinate-co-butylene adipate) by direct polycondensation of diols and diacids.

The limiting factors for a broader use of synthetic aliphatic polyesters derived from diols and diacids are their low mechanical and thermal properties. There is a need to synthesize chemically aliphatic polyesters with high molecular weight in order to improve their mechanical properties. Also, the incorporation of rigid aromatic structures into aliphatic copolyesters in the synthesis of polymers have improved the mechanical and the thermal properties with controlled biodegradability[16,18].

With regard to the high commercial potential of aliphatic-aromatic copolyesters and their interesting properties, in the present paper we report on the synthesis and characterization of high molecular weight random copolyesters poly(butylene adipate-co-butylene terephthalate), (PBAT) and poly(butylene sebacate-co-butylene terephthalate), (PBSeT) obtained by direct melt polycondensation of diols and diacids in the presence of a highly effective catalyst titanium tetraisopropoxide (TTiPO) have been discussed. The structure of their repeating units and the effect of the copolymer composition on the physical and thermal properties as well as enzymatic degradation were investigated. Lipase originating from *Candida cylindracea* was used in the degradation studies.

EXPERIMENTAL

Adipic acid (Merck AR grade), sebacic acid (Lancaster AR grade) and terephthalic acid (Lancaster AR grade) were recrystallized from deionized water and used. 1,4-Butane diol (Lancaster, AR grade) was dried with CaO overnight and then distilled under reduced pressure. Titaniam tetraisopropoxide, used as catalyst, purchased from Lancaster was used as such. *Candida cylindracea* lipase purchased from Sigma Aldrich was used for degradation experiment. All the other materials and solvents used were of analytical grade.

Synthesis of copolyesters: The copolyesters were synthesized by two step melt polycondensation method. As an example, the synthesis of poly(butylene sebacate-co-butylene terephthalate), PBSeT, has been described. The polycondensation flask was a three necked flask equipped with a nitrogen inlet, a condenser and a thermometer. A magnetic stirrer was used to stir the reaction mixture. The reaction mixture is 0.2 mol 1,4 butane diol, 0.1 mol sebacic acid and 0.1 mol terephthalic acid.

The reaction mixture is purged with nitrogen and heated in an oil bath. The temperature of the reaction mixture is raised to 150 ºC in 20 min. Then, the temperature is gradually raised in 10 ºC steps every minute to the final reaction temperature of 210 ºC to remove water being the esterification by product. When water ceased to be generated, a predetermined amount of titanium tetraisopropoxide (TTiPO) catalyst (0.1 mmol) was added to the reaction mixture. Subsequently, the pressure of the reaction system was gradually decreased and condensation polymerization was continued at 210 ºC under a final reduced pressure lower than 0.5 mm Hg. Finally, the reaction was terminated when the rotation of the mechanical stirrer is stopped. The viscous slurry was cooled in the flask under nitrogen atmosphere. The crude polyester was dissolved in chloroform and then poured into excess of dry cold methanol to purify the polyester. The precipitated polyester was dried in a dessicator to constant weight.

Gel permeation chromatography: The molecular weights of copolyesters were analyzed by gel permeation chromatography using a Shimadzu instrument equipped with a pump and a refractive index detector. Tetrahydrofuran was used as mobile phase with a flow rate of 1.0 mL/min. Polystyrene standards from shapodex were used for calibration.

Intrinsic viscosity: The intrinsic viscosity [η], of polymer solutions in chloroform was measured at 30 ºC in a constant temperature bath using Ubbelohde viscometer.

FT-IR: IR spectra of the copolyesters were recorded by Perkin-Elmer IR spectrometer in the range of 3800 to 400 cm^{-1}. The samples are embedded in KBr pellets.

Nuclear magnetic resonance (NMR): ^{1}H NMR spectra were obtained with a Jeol Model GS X 300 MHz NMR spectrometer using $CDCl_3$ and TMS as solvent and internal standard, respectively. The measurements were carried out at room temperature.

Differential scanning calorimetry (DSC): The DSC scans were recorded using a Perkin-Elmer Pyris I analyser. Indium was used as the calibration standard at a heating rate of 10 ºC/min.

X-ray diffraction (XRD): A Siemens D 500 diffractometer with CuK_α filtered radiation, was used for assessing crystallinity of the polymers. The samples were scanned over the range of 2θ angle, from 5º to 80º.

Enzymatic degradation: Copolyester films were obtained by hot pressing method above the melting temperature of the polyesters. The hot pressed films (10 × 10 mm^2 and *ca.* 200 µm thick) were incubated in duplicate at 30 ºC in separate petri dishes containing 7 mL of phosphate buffer ($pH = 7.00 \pm 0.01$) in the presence of the enzyme lipase from *Candida cylindracea*. The enzyme concentration was 1 mg/mL. The films were removed from the enzymatic solution after selected time intervals, washed with distilled water and dried under vacuum at room temperature to constant weight. This procedure was repeated for every chosen time interval: 9, 24, 48, 72 and 90 h. The extent of biodegradation was quantified using the weight loss and the initial sample weight[19,20]. A control test without enzyme was also carried out.

Scanning electron microscopy (SEM): The effect of biodegradation upon the polymer surfaces was examined using Jeol Model JSM-840A an SEM microscope. Prior to the analysis, the samples were coated with gold to avoid charging under the electron beam.

RESULTS AND DISCUSSION

Intrinsic viscosity, molecular weight and elemental analysis: Poly(butylene adipate-co-butylene terephthalate) (PBAT) and poly(butylene sebacate-co-butylene terephthalate) (PBSeT) were synthesized by a two step melt polycondensation method. The intrinsic viscosity, the molecular weights and the polydispersity index of the copolymers are presented in Table-1.

TABLE-1
INTRINSIC VISCOSITY AND MOLECULAR WEIGHT OF THE SYNTHESIZED POLYESTERS

Polymer	Intrinsic [η] (dl/g) viscosity	Mn (g/mol)	Mw (g/mol)	Mw/Mn
PBAT	0.80	10510	18025	1.71
PBSeT	1.02	19914	48194	2.42

The extent of the polymerization was determined by the molecular weight and the intrinsic viscosity of the polymers. High molecular weight is an essential requisite in order to achieve polymeric materials with sufficient mechanical properties. In all GPC measurements a single peak, which differs in magnitude and elution time, was observed. As shown in Table-1, the number average molecular weight (Mn) of the copolymers PBAT and PBSeT are 10510 and 19914 g/mol, respectively and the intrinsic viscosity, [η] are 0.80 and 1.02 respectively. In addition, the breadth of molecular weight distribution (Mw/Mn) was quite narrow for these polymers.

FT-IR and ^{1}H NMR: The structure of the repeating units of the polymers confirmed by means of elemental analysis, FT IR and NMR spectroscopy. The values obtained on elemental analysis for the resulting polymers were in good agreement with the calculated values for the proposed structures (Table-2).

TABLE-2
ELEMENTAL ANALYSIS

Polymer	Formula	Elemental analysis (%): Calcd. (Found)	
		C	H
PBAT	$(C_{22}H_{28}O_8)n$	62.92 (61.59)	6.92 (6.94)
PBSeT	$(C_{26}H_{36}O_8)n$	65.51 (64.12)	7.62 (7.48)

Absorption bands can be seen between 1730 and 1718 cm^{-1} show the presence of ester carbonyl group. Absorption bands at 1455-1410 and 875-731cm^{-1} are due to C-C stretching and C-H bending vibrations of aromatic ring. The C-H symmetric stretching of aliphatic $-CH_2-$ group is shown by absorption at 2954-2546 cm^{-1}. ^{1}H NMR spectra of the copolyesters are presented in Fig. 2.

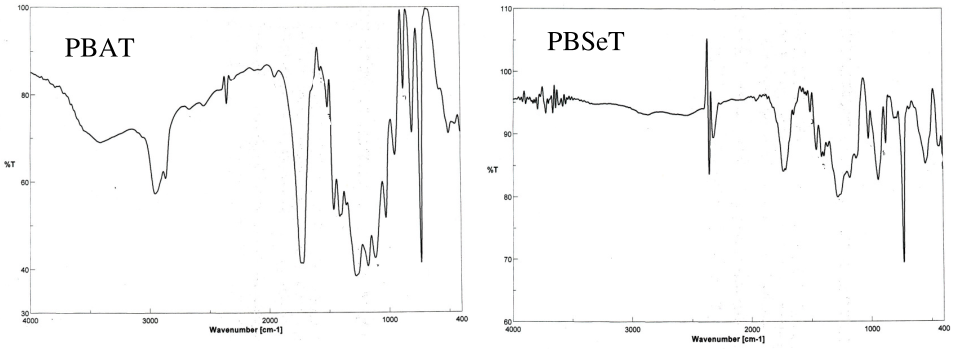

Fig. 1. IR Spectrum of PBAT and PBSeT

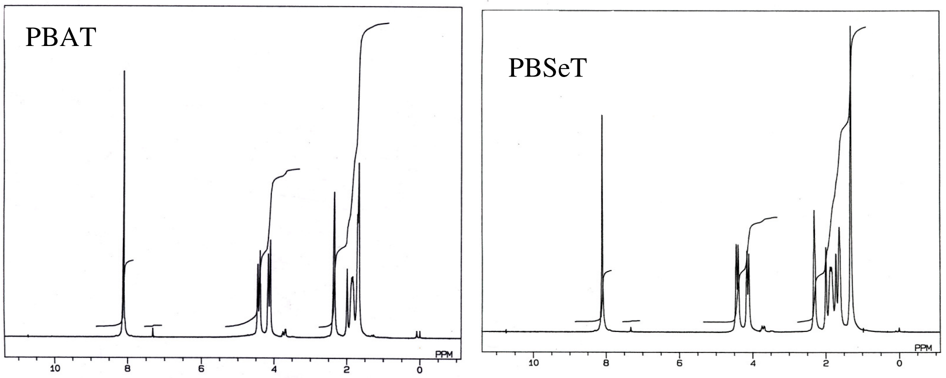

Fig. 2. ^{1}H NMR spectrum of PBAT and PBSeT

The peaks observed were attributed as follows; A singlet at δ = 8.1 ppm is due to aromatic protons of terephthalic group, multiplet at δ = 4.5-3.8 ppm is due to the protons of -CO-O-CH_2- group, multiplet at δ = 2.0-1.2 ppm is due to -CH_2-C-O group and a singlet at δ = 2.4 ppm is due to methylene protons of 1,4-butane diol.

Thermal properties: The results obtained from DSC analysis are summarized in Table-3. DSC thermograms of the synthesized copolyesters are shown in Fig. 3.

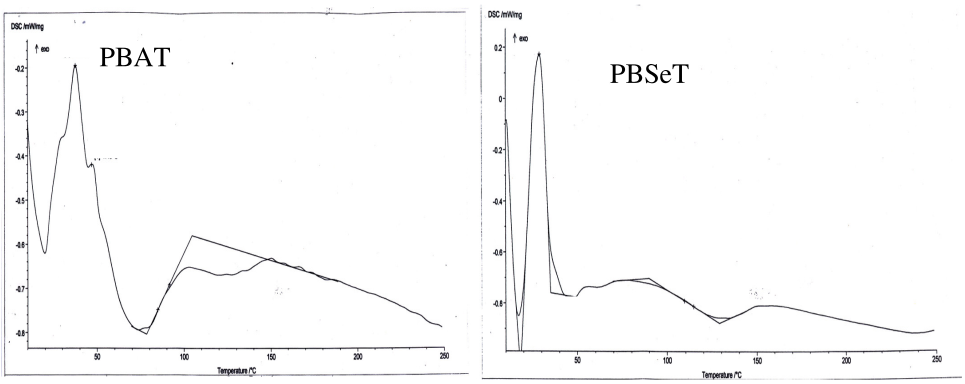

Fig. 3. DSC thermogram of PBAT and PBSeT

TABLE-3
THERMAL PROPERTIES OF THE SYNTHESIZED POLYMERS

Polymer	Tg (ºC)	Tm (ºC)	Td (ºC)	ΔHm (J/g)
PBABT	37.6	84.8	190.2	1.59
PBSeBT	29.0	114.4	210.4	1.49

PBSeT is a highly crystalline polymer exhibiting a melting point (Tm) of 114.4 ºC and a heat of fusion of 1.49 J/g while for PBAT, which is a less crystalline polymer, the corresponding values were 84.8 ºC and 1.59 J/g, respectively. The glass transition temperature (Tg) values of PBAT and PBSeT were 37.6 and 29 ºC, respectively. The glass transition temperature (Tg) of polymer is closely related to the flexibility of the chains because a high Tg is generally assumed to be connected with relatively high barriers of bond rotations[21]. When the length of the spacer group increases, it is observed on the thermogram that the glass transition temperature (Tg) values decreases. This can be attributed to the presence of more number of methylene groups in sebacate unit, which act as soft segments and decreases the Tg value of PBSeT.

X-Ray diffraction analysis: X-ray diffractogram of the synthesized polymers are shown in Fig. 4. Gaussian curves are used to describe the amorphous phase and crystal reflections of a diffractogram[22]. The intensity of diffraction peaks increases with the increase in the length of the flexible spacer group in the Fig. 4 of the diffractogram as reported by Chen *et al.*[23]. This indicates that the crystallinity of the polymer increases with the length of flexible segments.

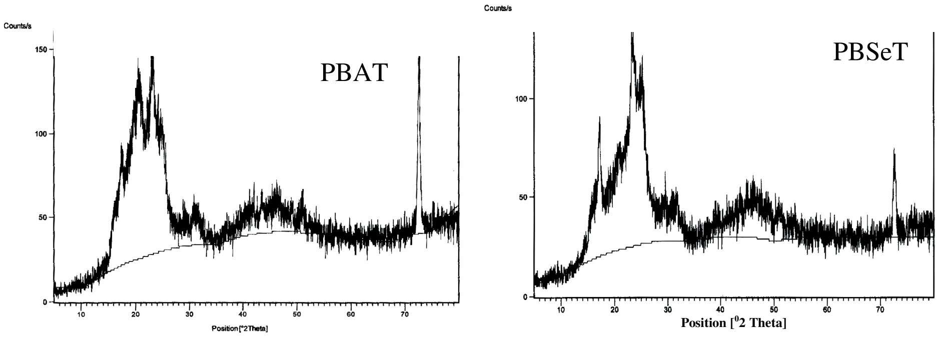

Fig. 4. X-Ray diffractogram of PBAT and PBSeT

Enzymatic degradation: In order to examine the biodegradability of the synthesized polyesters, enzymatic hydrolysis was carried out[24]. The enzyme lipase from *Candida cylindracea* was used for degradation test. The rate and degree of enzymatic degradation of aliphatic polyesters is usually related to their molecular weight, crystallinity and chemical structure of polyesters. The biodegradability of the copolyesters was determined by monitoring the weight loss or erosion of films with time. The time course of the enzymatic degradation of the polyesters during 90 h is shown in Fig. 5.

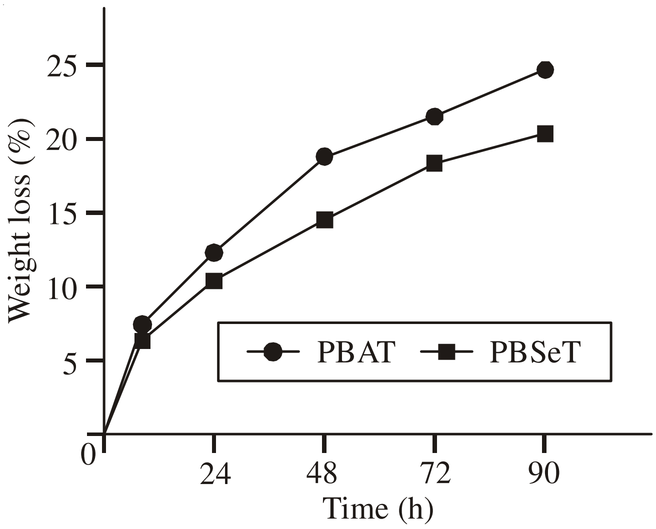

Fig. 5. Enzymatic degradation of polyesters PBAT and PBSeT

Before performing of the enzymatic degradation tests, hydrolytic degradation of the polyesters in the buffer solution without enzyme addition was carried out. The weight loss was almost negligible. Tokiwa and Suzuki[25] noted that the melting temperature of the polyesters has a great influence on the enzymatic hydrolysis of the polyesters by the enzyme *Rhizopus delemar* lipase. It is known that polymer degradation usually proceeds in a selective manner, with the amorphous regions being preferentially degraded as compared to crystalline ones[26]. In addition it seems that biodegradation does not significantly depend on polymer molecular weight which suggests that the enzyme used in this study belongs to the endo enzyme category. This type of enzymes randomly split bonds in the polymer chains and thus enzyme action is not affected by polymer molecular weight but by polymer chemical structure and crystallinity. Thus, the percentage weight loss of the copolyester PBAT was higher than the percentage weight loss for PBSeT.

Scanning electron microsopy (SEM): The effect of biodegradation upon the polymer surfaces was examined and confirmed by using SEM. As seen in the micrographs of Fig. 6, the hydrolytic action of the enzyme lipase from *Candida cylindracea* led to the formation of a rough surface with large cavities on the film surface.

Conclusion

The aliphatic-aromatic random copolyesters derived from terephthalic acid, 1,4-butane diol and adipic acid/sebacic acid were obtained by a two step polycondensation reaction in the presence of a highly effective catalyst titanium tetra isopropoxide at 210 ºC. The synthesized polyesters were characterized by thermal and spectral methods of analysis. The biodegradation of these polyesters are carried out using the enzyme lipase from *Candida cylindracea*.

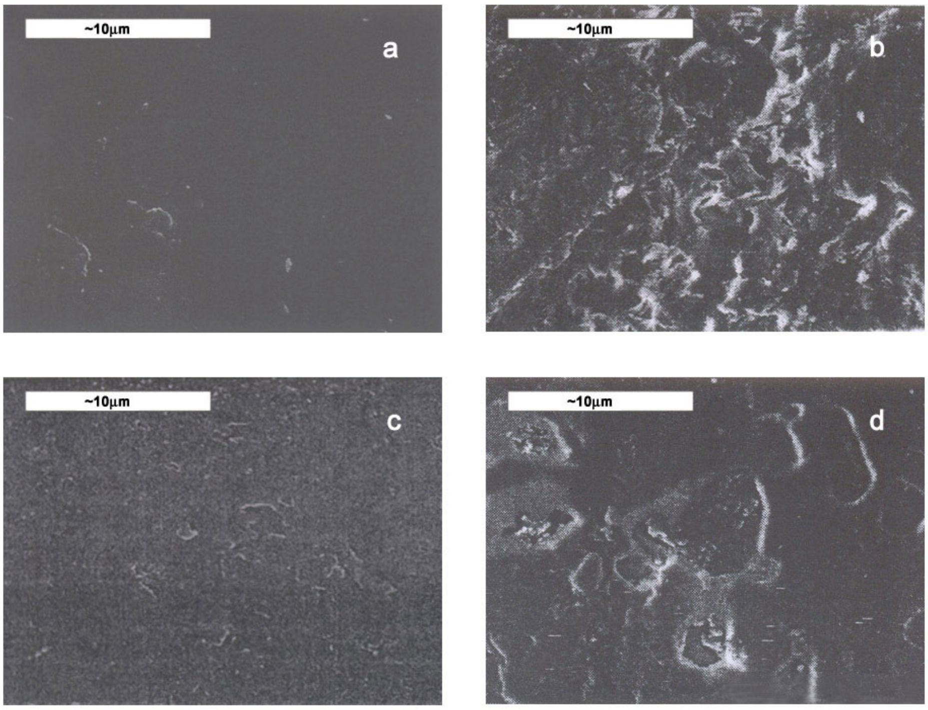

Fig. 6. SEM micrographs during enzymatic hydrolysis of polyester films (a), (b) before and after degradation of PBAT (c), (d) Before and after degradation of PBSeT

The results clearly indicate that the mobility of the polymer chains is the major and general controlling factor for the biodegrabdability of polyesters. Since it has been found that enzymes secreted by micro organisms to degrade the polyesters are of lipase type, the polyester chains must be mobile enough to reach the active sites of the lipase which are usually located rather deeply in a cavity of the protein structure and often covered by a lid-like structure[27]. The most important factor which controls the biodegradation rate is that how tightly the polymer chains are fixed in the crystalline regions of the material. This is characterized by the melting point of the material. Thus, the copolyester PBAT has higher degradation rate compared to PBSeT as the later being the high melting polymer. The results of this work demonstrate that the hydrolytic degradation of polyesters catalyzed by lipase enzyme is predominantly controlled by the overall thermal properties and crystalline nature of the material which inturn depend on the structure of the repeating units.

ACKNOWLEDGEMENT

The financial support of University Grants Commission, New Delhi, India is gratefully acknowledged.

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(*Received*: 5 June 2009; *Accepted*: 19 March 2010) AJC-8518